Surfactant structure and the thermodynamics of micelle formation

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SUMMARY

Surfactants are molecules which possess a dualistic character. They combine a water-preferring (hydrophilic) and a water-rejecting (hydrophobic) part in one molecule. This dualistic character is the basis of their surface activity. When surfactants are dissolved in water, the molecules may group together to form aggregates. In these self-assemblies the hydrophobic hydrocarbon tails tend to assemble, while their hydrophilic headgroups (and counterions) remain hydrated. A wide variety of aggregates (e.g. micelles or vesicles) may be formed, depending on surfactant structure, surfactant concentration, and temperature. This thesis deals with one of these types of aggregates, namely micelles. Micelles are important in industry and biology as a result of their solubilizing function: matter can be transported in aqueous solutions after it has been solubilized by the hydrocarbon interiors of micelles.

The size, shape and stability of micelles is strongly influenced by the molecular architecture of the surfactant. Surfactant monomers aggregate into spherical micelles above the critical micelle concentration (CMC). At higher surfactant concentrations, worm-like micelles are often formed. Highly concentrated surfactant solutions may exhibit lyotropic liquid-crystalline behavior. In the present study, the formation of various aggregates or phases has been examined using a variety of techniques: (i) conductometry (CMC and percentage of counterions bound to the micellar surface), (ii) microcalorimetry (CMC and information on interactions broken up or created in the course of micelle formation or micellar growth), (iii) NMR (micellar growth and counterion orientation/position), (iv) UV/VIS-spectroscopy (Krafft temperature and micellar catalysis), (v) optical polarization microscopy and differential scanning calorimetry (liquid-crystalline behavior), and (vi) theoretical thermodynamic models (prediction of micellar parameters).

This thesis deals with members of a family of cationic surfactants, namely the alkylpyridinium surfactants:

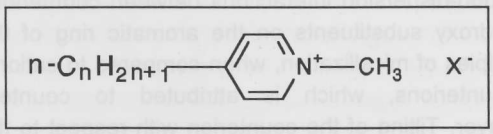

Chart 1. *Structure of alkylpyridinium surfactants.*

The hydrophobic part of the molecule consists of an alkyl chain (typically n=12), and the hydrophilic part consists of a pyridinium headgroup and counterions (X^-). This thesis mainly focuses on the influence of counterion structure on the aggregation behavior of alkylpyridinium surfactants, both in dilute and concentrated aqueous solution.

Surfactant chemistry is introduced in Chapter 1. This chapter focuses on micelles, either spherical or worm-like. Relationships between surfactant structure and the size, shape and stability of micelles in dilute aqueous solution and the type of lyotropic mesophase formed in

concentrated solutions are discussed. Furthermore, attention is paid to the driving force for micelle formation.

Chapter 2 describes the influence of counterions on the properties of micelles formed by 1-methyl-4-n-dodecylpyridinium surfactants. The critical micelle concentration, which is related to the Gibbs energy of micelle formation, increases upon increasing size of the hydrated counterion. Next to electrostatic interactions, also specific counterion effects are important with respect to micelle size, shape and stability. Factors which are to be considered are the position of the counterion at the micellar surface and the orientation of the counterion and its substituents with respect to the surfactant monomers in a micelle. The critical micelle concentration decreases upon increasing counterion hydrophobicity. 'Tilting' of the (aromatic) counterion with respect to the surfactant monomer in a micelle and introduction of o-methoxy substituents in aromatic counterions (i.e. the counterion becomes 'unsymmetric') results in higher critical micelle concentrations and lower degrees of counterion binding. Introduction o-hydroxy and p-chloro substituents in benzoate counterions, on the other hand, stabilizes the micelles to a marked extend. Now long, worm-like micelles are formed in dilute aqueous solution.

Fundamental issues of microcalorimetry are described in Chapter 3. The main conclusion which emerge from our studies are: (i) Surfactant solutions are thermodynamically nonideal, which can be demonstrated using microcalorimetry; (ii) measured enthalpies of micelle formation depend on surfactant concentration in the syringe and are independent of the stirring speed; (iii) measured enthalpies of micellization are not equal to standard enthalpies of micelle formation.

Structure/property relationships, with respect to the enthalpy of micelle formation, are explored in Chapter 4. The enthalpy of micelle formation, $\Delta_{mic}H$, becomes more exothermic upon increasing chain length of the alkyl chain, and decreasing headgroup size of the surfactant monomers. $\Delta_{mic}H$ is , within error limit, unaffected by the degree of branching of the alkyl chain of the surfactant. Analysis of the influence of counterions on measured enthalpies of micelle formation appeared to be more subtle. When only electrostatic interactions between counterion and headgroup are present, $\Delta_{mic}H$ becomes more exothermic upon increasing counterion size. p-Methyl substitution in aromatic counterions of surfactants results in more exothermic enthalpies of micelle formation due to enhanced London-dispersion interactions between counterions and surfactant monomers in the micelle. p-Hydroxy substituents on the aromatic ring of the counterion also result in more exothermic enthalpies of micellization, when compared to cationic surfactants with unsubstituted aromatic counterions, which is attributed to counterion(substituent)-water interactions in the Stern layer. Tilting of the counterion with respect to the surfactant headgroup or an unsymmetric nature of the counterion leads to less exothermic enthalpies of micellization.

Long, worm-like micelles are formed in dilute aqueous solution of 1-methyl-4-n-dodecylpyridinium surfactants containing either salicylate or p-chlorobenzoate counterions. Enthalpies of micellization are more exothermic for these surfactants than for surfactant forming spherical micelles.

The same Chapter describes a study of heat capacities of micelle formation, which are related to hydrophobic hydration, as a function of counterion structure. No trend was found with respect to this structural variable.

Enthalpies of micelle formation can also be calculated using thermodynamic models. These values were calculated using the phase-separation model, mass-action model and Poisson-Boltzmann model. Neither of the three model gave satisfactory agreements. Trends were predicted correctly, however, with respect to alkyl chain lengths and variations in branching of the alkyl chain.

Chapter 6 deals with the challenging phenomenon of micellar growth. Spherical micelles grow to form worm-like micelles at lower concentration upon: (i) Increasing counterion size; (ii) increasing counterion hydrophobicity; (iii) increasing counterion (substituent)- water interactions in the Stern layer.

Alkylpyridinium surfactants containing salicylate or p-chlorobenzoate as counterions form extremely long, worm-like micelles, which form entangled networks. Solutions of these surfactants are viscoelastic. This unusual unidirectional growth is hampered upon: (i) decreasing alkyl chain length and (ii) increasing headgroup hydrophobicity.
It is proposed that the orientation and microenvironment of the substituent in the aromatic counterion is of decisive importance for the observed properties.

At higher surfactant concentrations intermicellar interactions become important and liquid-crystalline phases are formed. Chapter 7 describes a preliminary study to the influence of the counterion on the liquid-crystalline behavior of alkylpyridinium surfactants. It is shown that the type and stability of the mesophases formed depend on the structure of the counterion.

Chapter 8 deals with micellar catalysis of the unimolecular decarboxylation of 6-nitrobenzisoxazole-3-carboxylate. Changes in catalytic efficiencies with the molecular structure of the micelle-forming surfactant are interpreted mainly in terms of initial state hydrogen bonding at the micellar binding sites.

In the final chapter the main findings and conclusions are summarized and discussed.